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(54) SYNERGISTIC BIOCIDAL COMPOSITIONS

(71) We, OLIN CORPORATION, a corporation organised and existing under the laws of the State of Virginia, United States of America, of 275 Winchester Avenue, New Haven, Connecticut, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

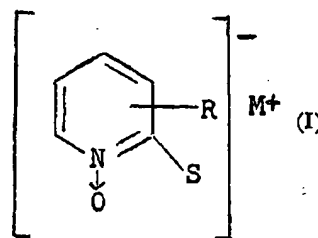
This invention relates to synergistic biocidal compositions having broad anti-bacterial and anti-fungal properties. More particularly, this invention provides a mixture of an alkali metal salt of a 2-mercaptopyridine-1-oxide, a water-soluble borate and one or more brominated salicylanilides.

Various synergistic mixtures containing 2-mercaptopyridine-1-oxides have been prepared and disclosed in the literature. For example, U.S. Patent Specification 2,909,459 discloses compositions comprising sodium 2-mercaptopyridine-1-oxide and a water-soluble borate, while synergistic mixtures of 2-mercaptopyridine-1-oxides and halogenated salicylanilides are disclosed in U.S. Patent Specification 3,235,455. Although these mixtures are effective in certain applications, there is a need for an economical biocidal composition which can be effectively employed in small amounts as a fungicide or bactericide.

Now it has been found in accordance with this invention that a selected ternary composition exhibits synergism when incorporated into a variety of media, thereby providing an economical, highly effective biocide.

More specifically, the synergistic biocidal compositions of this invention comprise 0.5 to 2.5% by weight of an alkali metal salt of a 2-mercaptopyridine-1-oxide, 85 to 97% by weight of a water-soluble borate and 1.8 to 10.0% by weight of a brominated salicylanilide.

The alkali metal salts of 2-mercaptopyridine-1-oxides employed in the compositions of this invention have the formula



wherein R is hydrogen, lower alkyl, i.e., alkyl having 1—5 carbon atoms, lower alkoxy or halo and M is an alkali metal, e.g., sodium, potassium, lithium, etc. The alkali metal salts of 2-mercaptopyridine-1-oxide, i.e., formula (I) wherein R is hydrogen, are preferred in the practice of this invention; sodium 2-mercaptopyridine-1-oxide has been found to be particularly efficacious.

Any water-soluble borate such as borax, i.e., sodium tetraborate, the tetraborates of potassium, lithium, etc., and the metaborates of the alkali metals can be employed in the composition of this invention. However, preferred embodiments utilize borax as the water-soluble borate.

Brominated salicylanilides suitable for use in the composition of this invention include 3,4,4'-tribromosalicylanilide, 3,4',5-tribromosalicylanilide, 4',5-dibromosalicylanilide, 5-bromosalicylanilide, 3,5-dibromosalicylanilide, 2',5-dibromosalicylanilide, 2',3,4',5-tetrabromosalicylanilide, 2',3,5-tribromosalicylanilide, 3',4',5-tribromosalicylanilide, 4',4',5-tribromosalicylanilide, 3,3',4',5-tetrabromosalicylanilide, 2',3,4',5,5'- and 2',3,4',5,6'-pentabromosalicylanilide and mixtures thereof. Particularly preferred are mixtures comprising about 45% by weight 3,4',5-tribromosalicylanilide, about 45% by weight 4',5-dibromosalicylanilide and about 10% by weight of other brominated salicylanilides.

The compositions of this invention are provided by admixing the aforementioned ingre-

dients in the appropriate amounts.

The synergistic biocidal compositions of this invention have a variety of useful applications. Thus, for example, they are used to inhibit fungal and bacterial growth in gypsum-based dry-wall cements, soaps and floor polishes.

These compositions are also effective slimicides for paper; in this application they are admixed with starch and applied to the paper during the sizing operation.

While the biocidal effect of the synergistic compositions of this invention is observed over a wide range of biocide concentration, generally from 200 to about 6000 ppm, and preferably from about 1000 to about 3000 ppm is employed. Greater and lesser amounts can be utilized and the ranges set forth herein are not intended to be limited.

The following examples will serve to illustrate the practice of this invention.

Examples

A series of one pint paint containers were provided with 400 grams of a 10% by weight aqueous solution of casein containing enough ammonia to aid in the dispersion of the casein. Varying amounts of biocide as indicated below were added and the respective containers closed, allowed to stand at room temperature and opened at intervals and inspected. Spoilage was indicated by a strong odor. In the Table, NaMPO indicates sodium 2-mercaptopyridine-1-oxide while *Temasept* (Trade Mark) refers to a mixture comprising about 45% by weight 3,4',5-tribromosalicylanilide, about 45% by weight 4',5-dibromosalicylanilide and about 10% by weight of other brominated salicylanilides as produced by Fine Organics Inc. F indicates failure had occurred at number of days stated; + indicates failure has not occurred yet at the indicated number of days.

Ex.	Preservative (ppm)			Number of Days Preserved	
	Na MPO	Borax	Temasept		
	(Na ₂ B ₄ O ₇ · 10H ₂ O)				
1	25			F	35
2		25		F	6
3		2500		F	32
4			25	F	6
5			1000	F	12
6	25	+	2500	F	105
7	25	+	225	F	between 756—790
8		1500	+	50	F between 186—209
9		2500	+	50	F between 294—334
10	25	+	1000	+	813
11	25	+	2500	+	813
12	50	+	2500	+	813
13	15	+	1000	+	813
14	15	+	1000	+	813

The examples summarized in the Table above show conclusively that the compositions in accordance with this invention display marked synergistic biocidal effects. Thus, in Example 6, a composition comprising 25 ppm

Na MPO and 2500 ppm borax failed at 105 days; in Example 7 the mixture of 25 ppm NaMPO and 225 ppm Temasept had failed at less than 790 days; while in Example 9, a composition comprising 2500 ppm borax and

50 ppm Temasept failed at less than 334 days. Thus, a composition comprising the sum of these mixtures would be expected to fail at 105+790+334, or 1229 days. Following the same reasoning, a composition comprising 1/2 of the sum of the ingredients contained in Examples 6, 7 and 9 would be expected to fail at 1229/2 or 615 days. However, Example 11, comprising 25 ppm Na MPO, 2500 ppm borax and 100 ppm Temasept had not failed when last inspected at 813 days. Similar analogies can be drawn from Examples 10, 12, 13 and 14 to indicate the synergism of the ternary compositions of this invention.

15 WHAT WE CLAIM IS:—

1. A synergistic biocidal composition comprising 0.5 to 2.5% by weight of an alkali metal salt of 2-mercaptopyridine-1-oxide (which may be substituted on the ring by a

C₁ to C₈ alkyl radical, a C₁ to C₈ alkoxy radical or a halogen atom), 85 to 97% by weight of a water-soluble borate and 1.8 to 10.0% by weight of a brominated salicyl-anilide.

2. The synergistic biocidal composition of Claim 1 wherein borax is employed as the water-soluble borate.

3. The synergistic biocidal composition of Claim 1 or 2 wherein sodium 2-mercaptopyridine-1-oxide is employed as the alkali metal salt of 2-mercaptopyridine-1-oxide.

4. The synergistic biocidal composition of Claim 1 substantially as hereinbefore described in any of the Examples.

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